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CHEMICALS IN MATERIAL CYCLES

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SUMMARY: Material recycling has been found beneficial in terms of resource and energy performance and is greatly promoted throughout the world. A variety of chemicals is used in materials as additives and data on their presence is sparse. The present work dealt with paper as recyclable material and diisobutyl phthalate (DiBP) as chemical in focus. The results showed variations, between 0.83 and 32 μg/g, in the presence of DiBP in Danish waste paper and board and potential accumulation due to recycling.

1. INTRODUCTION

Recycling of materials has been greatly promoted as it puts less pressure on natural resources and energy uses in the society. Once a product is recycled, it substitutes products based on virgin materials – hence avoiding extraction of additional resources. It has also been shown that recycling may consume less energy as compared with processing of raw materials (e.g. Villanueva and Wenzel, 2007). In this context recycling promotes sustainable consumption while offering environmental benefits when compared to conventional production practices. Taking advantage in these benefits has been reflected in current European (Waste Framework Directive, 2008/98/EC) and national waste and resource strategies (e.g. Danish Goverment, 2013), where increase in recycling rates is greatly promoted. On the other hand, need for enhanced physical properties, functionality, and appearance resulted in increasing complexity of products. Assuring such complexity is mostly done through improved design (e.g. composites) or addition of chemicals. Such chemicals, i.e. additives, improve not only the properties and characteristics of products but also the efficiency of production and manufacturing processes. Types and quantities of chemicals added depend on the material being processed (e.g. plastics, paper, wood, etc.) as well as the final application of the product (e.g. packaging, information transfer, construction, etc.). Examples of additives can be printing inks, glues, solvents, and plasticizers. The information of the amounts of chemicals added to materials or even the kind of chemicals added is often sparse in the literature (e.g. Pivnenko et al., 2015), and may represent a limiting factor in assessing the implications of their presence.

Part of a recycling process is a pre-treatment of waste materials in order to remove potential physical and chemical contamination. Since such treatments cannot guarantee 100% efficiency (BMELV, 2012), the chemicals may persist in the process and be re-introduced into the material cycles. This may lead to inferior quality of products made from recycled waste materials and jeopardize the general acceptance of recycled products. The issue of quality in recycling has been previously voiced (Velis and Brunner, 2013) and the authors called for alternative recycling performance indicators and further research.

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Although chemicals added to materials are regulated under the current EU legislation, i.e. Regulation concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH, 1907/2006/EC), the chemicals indirectly added through recycling are poorly regulated (Lee et al., 2014). According to REACH, 20 % impurities (including additives) carried over with recycled secondary raw material are allowed without further restrictions. This “gap” in legislation may allow contamination of consumer products with micropollutants, i.e. chemicals present in “low concentrations”, if use of recycled materials is to be promoted.

Paper is the most recycled packaging material in Europe, with more than 81% recycling rate in 2011 (CEPI, 2013a). Even if the figures are extended beyond packaging, paper can be one of the most recycled consumer materials. Paper may also contain a variety of chemicals either added intentionally to the material or being part of the contamination that may occur either through use or waste collection phases (Pivnenko et al., 2015). Once paper is recycled, chemicals may persist in the process and, unless removed or degraded, might end up in the final paper product (Biedermann et al., 2011) putting the quality of material at stake.

Phthalates are commonly used in a variety of products, including plastics and paper. In paper they are mostly used as plasticizers in ink and glue preparation (Pivnenko et al., 2015). Some of the phthalates used are classified as Endocrine Disrupting Chemicals (EDCs), drawing increasing attention to their presence in conventional consumer products. Some of the phthalates (e.g. diisobutyl phthalate, DiBP) have been classified as substances of very high concern (SVHC) and are subject to authorization in accordance to REACH. Nevertheless, the gap in the legislation, mentioned above, will allow their presence in consumer products through recycling even after being phased out from use.

The aim of the work was to gain a better and quantitative understanding of the presence of chemicals in materials with the example of paper as material and diisobutyl phthalate (DiBP) as chemical in focus. The manuscript reports preliminary data for work in progress.

2. MATERIAL AND METHODS

2.1 Waste paper

Samples of waste paper were collected from a municipality in Southern Denmark. Samples represent source-segregated household waste paper flow collected separately from the residual waste and intended for recycling. After sampling, waste paper was manually sorted into 10 fractions (5 paper and 5 board fractions) and stored in individual paper sacks. The fractions were defined as described in Table 1.

After been collected and sorted, the paper samples were treated accordingly in order to homogenise the material within each fraction and allow chemical analysis to be performed. The pre-treatment of the samples included coarse shredding (ARP SC2000, Brovst, Denmark), fine shredding to particle size less than 4 mm (SM2000, Retsch, Germany), and lyophilisation, before being stored at -20°C in individual sealed glass containers.

Table 1. Fraction of waste paper sorted in the present study.

#	*Fraction*	*Brief description*
	Paper	
1	Flyers	Printed media advertising goods or services
2	Newspapers & Magazines	Newspapers and glossy magazines
3	Office & Administrative paper	Office paper, books, envelopes, books, booklets, etc.
4	Paper packaging	Wrapping paper and kraft brown and bleached paper
5	Miscellaneous paper	Other paper not included in the fractions above
	Board	
6	Corrugated board	Items of corrugated board used e.g. for shipping or product packaging
7	Paperboard	Items of paperboard used e.g. for shipping or product packaging
8	Other board packaging	Board packaging not included in the fractions above (e.g. egg trays, beverage cartons, etc.)
9	Paper tableware	Disposable plates, cups, etc.
10	Miscellaneous board	Other board not included in the fractions above

2.2 Chemical analysis

One sample from each paper fractions defined in section 2.1 was analysed for presence of DiBP.

Sample aliquots of 1.5 g of dried and pulverized paper and board were mixed with 20 ml ethyl acetate. After being agitated for an hour by a shaker, samples passed through a solid phase extraction column for a clean-up. The flow-through was collected, evaporated to approx. 3 ml and analysed on a gas chromatograph (GC) paired with a mass spectrometer (MS). The limit of detection achieved was 0.056 μg/g, and recovery, based on replicates of spiked paper samples, was 118%. The results were not corrected for the recovery.

3. RESULTS AND DISCUSSION

3.1 Waste paper composition

The composition of the waste paper sample collected is presented in Table 2. The vast majority of the sample was represented by paper (87.3 %), as opposite to the board (12.7 %). The largest share of paper (56.1 %) was classified as advertising material, while newspaper and magazines represented the second largest fraction (26.7 %). On the other hand, most of the board collected could be attributed to packaging (e.g. shipping) with corrugated board having the largest share (8.3 %).

Table 2. Composition of the source-segregated waste paper sample collected

#	*Fraction*	*Weight distribution [%]*
	Paper	87.3
1	Flyers	56.1
2	Newspapers & Magazines	26.7
3	Office & Administrative paper	4.1
4	Paper packaging	0.3
5	Miscellaneous paper	0.1
	Board	12.7
6	Corrugated board	8.3
7	Paperboard	2.9
8	Other board packaging	0.9
9	Paper tableware	<0.1
10	Miscellaneous board	0.6
	Total	100

3.2 Diisobutyl phthalate concentrations and amounts in paper waste

Concentrations of DiBP found in the fractions of waste paper and board analysed are shown in Figure 1. All samples showed quantifiable levels of the DiBP. It is evident that corrugated board contained the highest concentrations of the chemical in focus. Among the paper samples, the paper packaging showed the highest concentration, followed by office & administrative and miscellaneous paper. Among all the samples quantified, paper tableware, flyers, newspaper and magazines exhibited the lowest concentrations of DiBP.

The concentrations found are within the range between 2.2 and 120 μg/g, reported in the literature (Pivnenko et al., 2015). Wide occurrence of the chemical in paper and board is evident from the present study, as well as e.g. study conducted by Fierens et al. (2012) who found DiBP in 75 % of the 400 paper packaging samples analysed. Similarly Poças et al. (2010) found the chemical in concentrations between 0.15 and 21 μg/g in almost all the samples analysed.

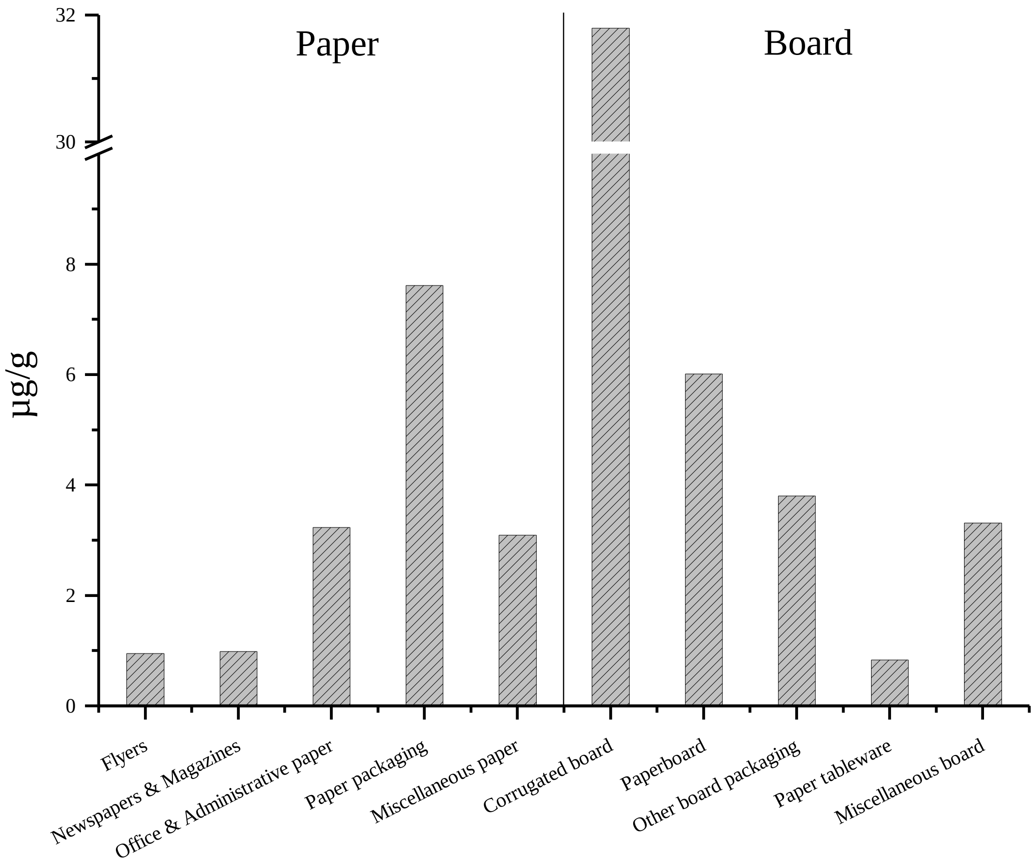

Figure 1. Concentration of diisobutyl phthalate (DiBP) in the source-segregated waste paper and board (µg/g dry weight).

The distribution of DiBP in the different fractions of the household waste paper is illustrated in Figure 2. The distribution was based on waste paper composition (Table 2) and concentrations of DiBP in the respective fractions (Figure 1). It is evident that the majority (70 %) of DiBP in the Danish source-segregated waste paper sent for recycling was in corrugated board fraction.

This fraction mostly contained board packaging, which was expected to have high content of recycled fibres, since presence of recycled paper in European board packaging can even on average get up to 94 % (CEPI, 2013b). Such high recycling rates could potentially explain the high concentration of the phthalate in the fraction, although direct use of it as additives in some items ending up in the fraction could not be eliminated.

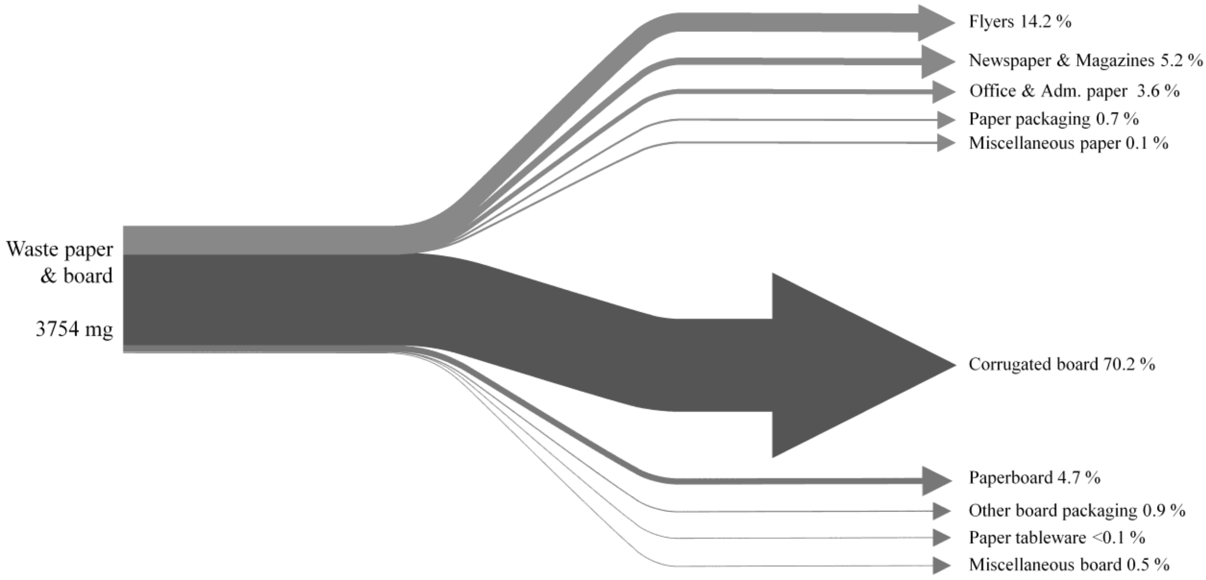

Figure 2. Distribution of diisobutyl phthalate (DiBP) in 1000 kg of waste paper and board.

3.3 Paper cycle

A generic mass flow of European paper cycle is presented in Figure 3. It is evident from the figure that chemicals might be introduced into the cycle in a variety of steps (e.g. paper production, paper conversion, etc.). Most probable step remains paper conversion, as the largest amounts and diversity of chemicals are added to the paper there (Pivnenko et al., 2015).

It is also evident from the figure that chemicals present in the waste paper being recycled might be re-introduced into the newly manufactured paper products. Poças et al. (2010) also mentioned recycled pulp as important source of phthalates in paper and board packaging, while Lee et al. (2014) suggested increased exposure to phthalates of 2-year-old children due to waste paper recycling.

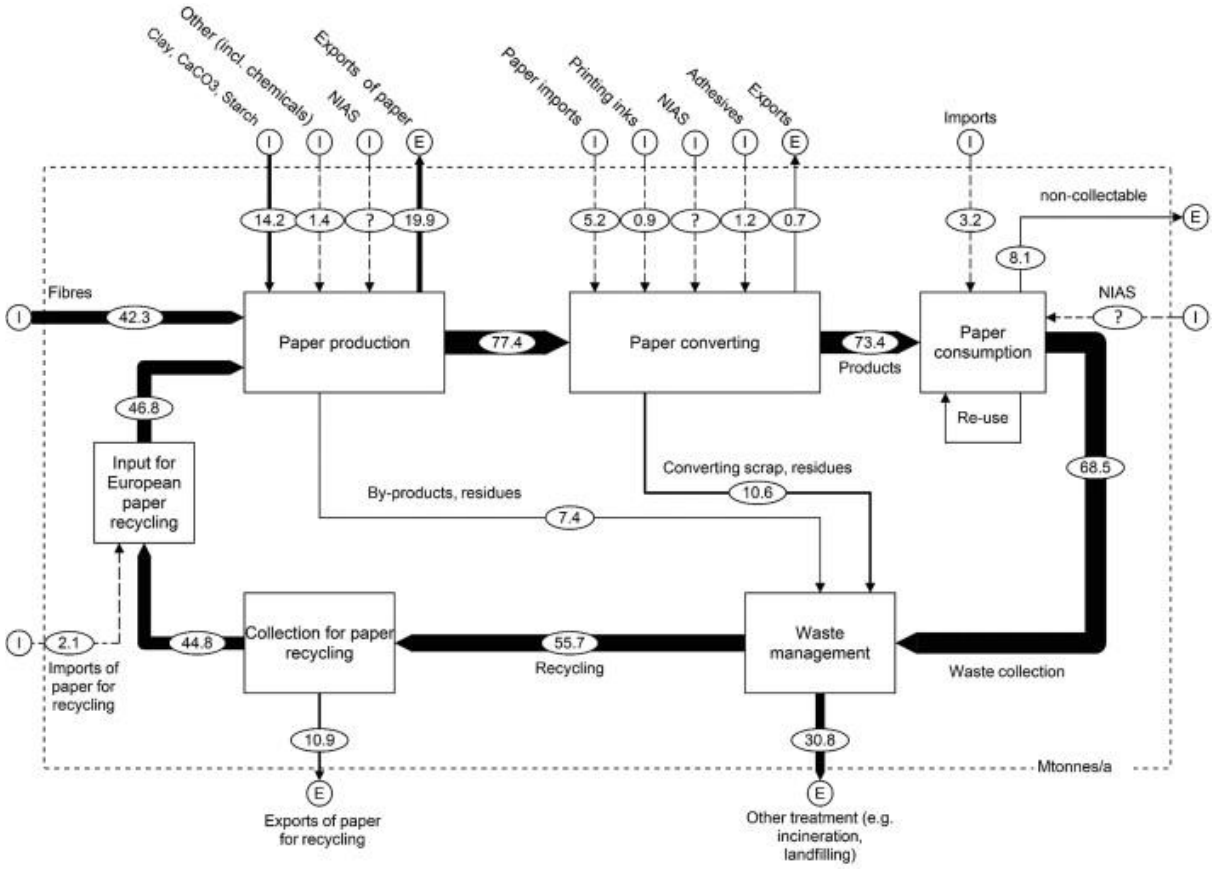

Figure 3. European paper cycle (Pivnenko et al., 2015). Dashed lines represent chemicals “entry points”.

4. CONCLUSIONS

Source-segregated waste paper and board contained mainly flyers, newspapers & magazines, and corrugated board, representing more than 91 % of the sample collected. DiBP was present in all the waste paper fractions quantified, with corrugated board showing the highest concentrations.

When waste paper and board composition and concentrations measured were combined, corrugate board was shown to represent the largest share of the mass flow of DiBP in the waste paper and board sent for recycling. The results indicate potential accumulation of the chemical due to recycling, as the content of recycled paper in the fraction was expected to be high.

High recycling rates associated with paper production in Europe and potentially high number of chemicals added in paper production and conversion may result in accumulation of chemicals and their presence in the newly manufactured products. More data on presence of chemicals in materials will be required in future in order to have a better understanding of their impact on the material recycling.

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